Studies of ozone depletion and its effects

Photoinhibition in antarctic phytoplankton by ultraviolet-B radiation in relation to column ozone values

OSMUND HOLM-HANSEN, VIRGINIA E. VILLAFAÑE, *and* E. WALTER HELBLING, *Polar Research Program, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093-0202*

Since the seasonal depletion of ozone over Antarctica was documented a few decades ago, researchers have speculated on the impact of the increasing ultraviolet radiation (UVR) on rates of primary production by antarctic phytoplankton and the ensuing effects on the marine ecosystem (El-Sayed 1988; Weiler and Penhale 1994). Results from *in situ* incubations with radiocarbon have been used to estimate the potential loss of primary production due to solar UVR to the marine ecosystem on the seasonal or annual basis. Of special concern were effects of enhanced ultraviolet-B (UV-B) radiation [280–320 nanometers (nm)] that result from depletion of atmospheric ozone. These estimates of loss of primary production due to enhanced UV-B radiation have been based either on the action spectrum for photoinhibition coupled with the changed in incident spectral irradiance as a function of column ozone values (Holm-Hansen, Helbling, and Lubin 1993) or on measurements made in the presence or absence of an ozone hole (Smith et al. 1992). Neither of these reports, however, included the weather conditions for the estimates of the percentage of carbon loss due to UV-B radiation.

The degree of cloudiness, which is independent of column ozone values, can have dramatic effects on incident spectral irradiance and hence on the magnitude of photoinhibition by UVR. To improve our understanding of the relationships between column ozone values, incident UVR, and magnitude of inhibition of photosynthesis in antarctic phytoplankton, studies were carried out at Palmer Station on Anvers Island (64.8°S 64.1°W) in October, November, and December of 1993 and 1994, which is the seasonal period for the most pronounced development of the ozone hole in the Antarctic. Because the ozone hole is sporadic and has alternating periods of low and high column ozone values, our daily incubations allowed us to study the relationship between degree of photoinhibition and the column ozone values prevailing during the incubations.

Water samples were obtained daily from Arthur Harbor, and the natural phytoplankton assemblages were incubated for 6–10 hours (centered around local apparent noon) with radio-labeled bicarbonate in temperature-controlled water baths that were exposed to direct solar radiation. Samples were contained in 50-milliliter quartz glass tubes, and triplicate samples were taken for each of the three treatments:

- with no pre-filter, so samples were exposed to photosynthetically available radiation (PAR; 400–700 nm) as well as UV-A (320–400 nm) and UV-B radiation;
- with a mylar pre-filter so that cells were exposed to PAR plus UV-A; and
- with a Plexiglas UF3 filter so that cells were exposed only to PAR.

After the incubation period, samples were filtered through glass fiber filters (Whatmann GF/F, 25-millimeter), any residual inorganic carbon was eliminated by exposure to acid fumes, and the fixed radiocarbon was measured in a liquid scintillation counter.

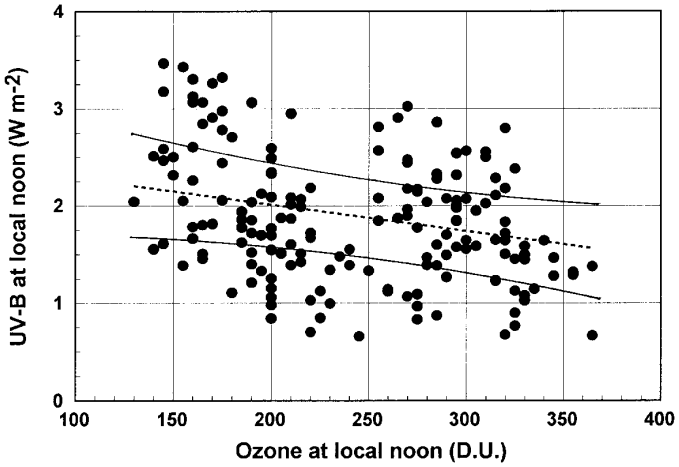
The column ozone values during the 83 experimental incubations ranged from 130 to 365 dobson units (DU). Results and statistical evaluations for all experiments, which were divided into three groups based on the column ozone values during the incubation (<200 DU, 200–300 DU, and >300 DU), are shown in the table. The mean values for column ozone and those of the ratio of radiation at 305 nm/340 nm were different for each of the three groups. The values for the UV-B irradiance at noon for groups A and C are significantly different, but groups A and B are not significantly different, nor are groups B and C. There were no statistically significant differences between any of the three groups in regard to UV-A irradiance, PAR, or the magnitude of inhibition due to either UV-A or UV-B radiation. As effects of ozone concentrations in the stratosphere should affect only UV-B radiation, it is to be expected that there would be no differences in UV-A or PAR radiation as a function of column ozone values.

To find no statistically valid differences in the magnitude of photoinhibition by UV-B radiation under varying column ozone values is surprising. Data in the figure show the relationship between UV-B radiation during all our experiments as a function of the column ozone values. The mean square fit for these data shows a slight negative slope, as would be expected. Most of the data points, however, are scattered outside of the 95 percent confidence limits. This scatter for the data reflects the extremely variable cloud cover that is characteristic of the marine environment in the Antarctic. The significance of this cloudiness in regard to effects of UV-B radiation on phytoplankton is that it largely obscures the effects of

The effect of varying column ozone levels on incident solar radiation and the inhibition of photosynthesis by UVR at Palmer Station, Antarctica

Variable	Ozone concentration[a]						Probability	Nemenyi[b]
	<200 DU		200–300 DU		>300 DU			
Ozone[a c]	180	(13)	263	(18)	336	(16)	p<0.0001	Ā B̄ C̄
UV-B[a c]	2.15	(0.5)	1.74	(0.5)	1.43	(0.4)	p<0.001	Ā B̄ C̄
UV-A[a c]	32.8	(10.1)	32.7	(14.2)	32.6	(9.6)	p>0.9	Ā B̄ C̄
PAR[a c]	159	(54.7)	160	(71.3)	159	(54.3)	p>0.9	Ā B̄ C̄
305 nm/340 nm[a d]	3.7	(0.6)	1.8	(0.4)	0.95	(0.3)	p<0.0001	Ā B̄ C̄
Inhibition by UV-B[a e]	15.7	(6.5)	14.5	(10)	12.8	(6.8)	p>0.2	Ā B̄ C̄
Inhibition by UV-A[a e]	28.6	(11.6)	30.4	(18.2)	29.9	(16.3)	p>0.9	Ā B̄ C̄

[a]Data show the mean values and standard deviations (in parentheses) of total ozone column values (in dobson units), UV-B (in watts per square meter), UV-A (in watts per square meter), PAR (in watts per square meter), ratio of energy at 305 nm/340 nm (× 100), inhibition by UV-B (percentage), and inhibition by UV-A (percentage) when grouped under three different conditions of ozone concentration.
[b]A, <200 DU; B, 200–300 DU; C, >300 DU.
[c]The data for ozone, UV-B, UV-A, and PAR were at local noon and were obtained from the National Science Foundation Monitoring Network at Palmer Station.
[d]Data for the ratio of energy at 305 nm/340 nm were obtained from the PUV-510 radiometer.
[e]Data for the percent inhibition caused by UVR are from the 83 standard tests done at Palmer Station in 1993 and 1994.



Noontime values of UV-B irradiance at Palmer Station as a function of column ozone values. The 83 points are from days during which photoinhibition experiments were performed at Palmer Station during October, November, and December of 1993 and 1994. The dashed line is the mean-square fit; the curved lines represent the 95 percent confidence limits. The data for UV-B and ozone were obtained from the National Science Foundation monitoring Network at Palmer Station. (W m^{-2} denotes watts per square meter.)

enhanced UV-B radiation, which should be positively correlated with variations in column ozone values. This effect of clouds should be taken into account for future modeling efforts that estimate or predict photobiological effects due to the ozone hole on the antarctic marine ecosystem.

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Correlations between ozone loss and volcanic aerosol at altitudes below 14 kilometers over McMurdo Station, Antarctica

TERRY DESHLER *and* BRUNO NARDI, *Department of Atmospheric Science, University of Wyoming, Laramie, Wyoming*
DAVID J. HOFMANN *and* BRYAN J. JOHNSON, *National Oceanic and Atmospheric Administration, Boulder, Colorado*

The aerosol content of the winter polar stratosphere has a significant impact on ozone loss due to heterogeneous chemistry involving chlorine reservoirs and polar stratospheric cloud (PSC) particles. In addition, mounting evidence indicates that ozone loss can also be initiated through heterogeneous reactions on sulfuric acid aerosol after major volcanic eruptions (Hofmann and Solomon 1989; Rodriguez et al. 1994). Here we present measurements, taken from late August to October in the lower stratosphere over Antarctica, of ozone and volcanic aerosol spanning the years 1986–1995. The measurements were made using balloonborne instruments.

In situ aerosol measurements began in Antarctica in the 1970s but switched from austral summer to the August-through-October period beginning in 1986. During the years 1986–1990, aside from PSC activity, the stratospheric aerosol can be characterized as being at background levels (Hofmann 1990), which persisted over Antarctica until late September 1991 when aerosol arrived from the volcanic eruptions of either Mount Pinatubo in the Philippines (June 1991) or Mount Cerro Hudson in Chile (August 1991) (Deshler et al. 1992). Prior to the advent of the volcanic aerosol, the background aerosol profiles from year to year were quite consistent. The 1990 and early 1991 profiles characterize this period.

Aerosol mass and surface areas were calculated from the aerosol measurements for each non-PSC aerosol flight. The evolution of the stratospheric aerosol during the period encompassing the eruption of Mount Pinatubo is indicated by the vertical profiles of aerosol surface area shown in figure 1. The increase observed in 1991 was confined to altitudes from 10 to 13 kilometers (km) and was observed to persist throughout the vortex after the middle of September (Deshler et al. 1992). By the onset of the winter vortex in 1992 the Mount Pinatubo aerosol was globally distributed and surface-area increases were observed up to 20 km in September 1992. Little aerosol was observed above this altitude probably because of the wintertime subsidence. In 1992, surface-area densities had maxima of near 30 microns per cubic centimeter ($\mu m^2\ cm^{-3}$) at 12–15 km, decreasing to 15–25 $\mu m^2\ cm^{-3}$ by 1993. By 1994, surface-area densities were within a few percentages of the pre-Pinatubo back-

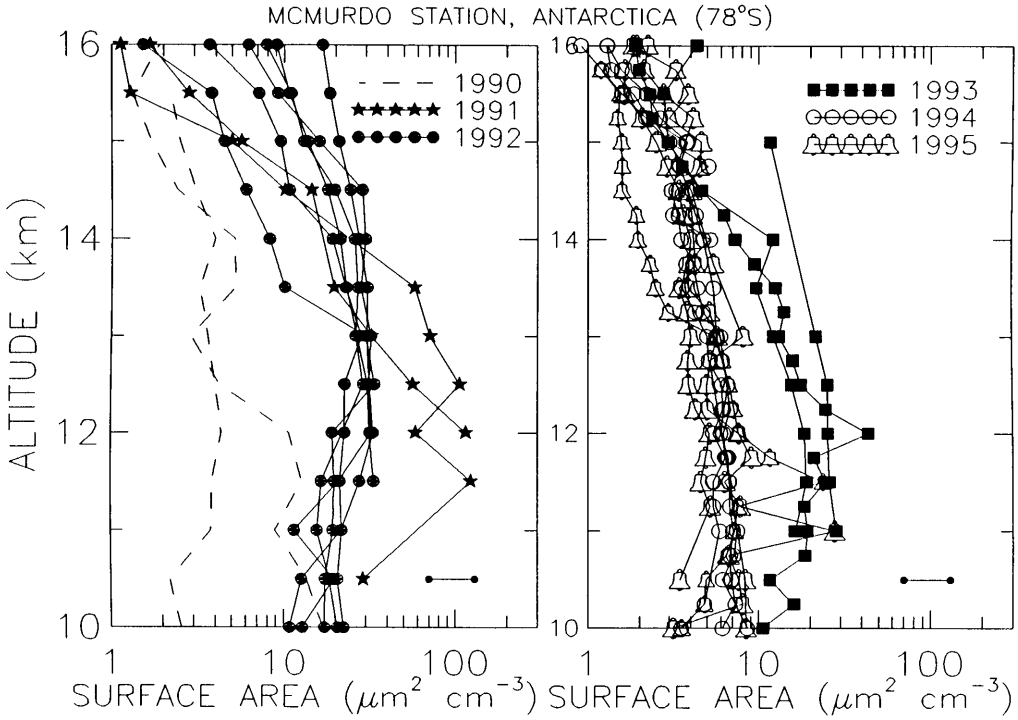

Figure 1. Vertical profiles of aerosol surface area density 1990–1995, calculated from size distributions fitted to the aerosol measurements. The uncertainty in the surface area is estimated to be ±30 percent indicated by the error bar in the lower right corner.

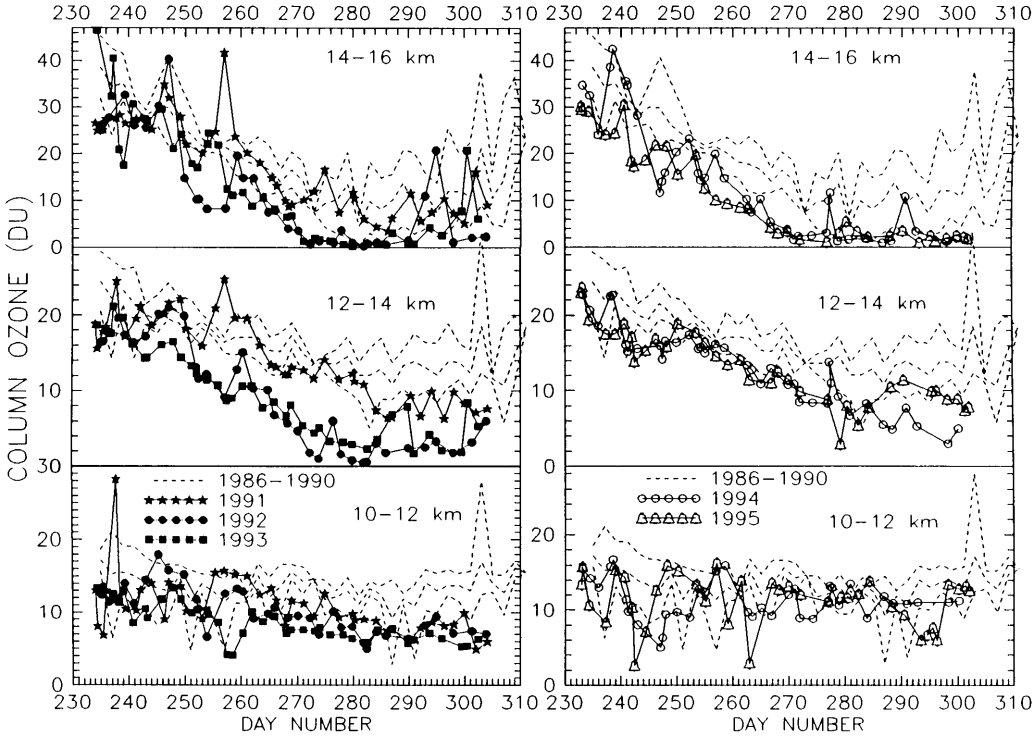

Figure 2. Column ozone in 2-km layers, 10–16 km, over McMurdo late August through October for the years 1986–1995. The 1986–1990 data are shown as an average and range of the measurements. The 1991–1993 measurements are in the left-hand panel; the 1994 and 1995 measurements are in the right-hand panel.

ground. Little change was observed between 1994 and 1995. Based on these measurements, the volcanic aerosol signal persisted for just 3 years, corresponding to an exponential decay time of 420 days.

It is now well known that chlorine-catalyzed ozone loss over Antarctica is controlled by the occurrence of PSCs, which are required to transform the inorganic chlorine reservoir into free radicals. In support of this idea, the majority of ozone loss over McMurdo has been observed only between 12 and 20 km (Johnson, Deshler, and Zhao 1995), the altitude range where PSCs are also observed. Thus, below 12 km, very little ozone loss has been expected. Column ozone in 2-km layers from 10 to 16 km is shown for the years 1986–1995 in figure 2. Clearly, only minimal ozone loss was observed below 12 km prior to 1991, whereas between 12 and 14 km, ozone loss is significant: on the order of a 50 percent decrease through the observing period in 1986–1990. Even greater loss, up to 70 percent, is observed between 14 and 16 km, a region at the lower boundary of the coldest temperatures in August and September and, thus, a region of significant PSC activity. Comparing the 1986–1990 ozone column amounts with the 1991–1993 measurements shows a fairly clear pattern of declining ozone at the lower levels for 1991–1993. This pattern began in late September 1991 coinciding with the arrival of the volcanic aerosol in the lower regions of the polar vortex and is evident between 10 and 14 km but not above 14 km where the volcanic aerosol did not penetrate. Both 1992 and 1993 were record years for ozone loss between 10 and 14 km. In both years, ozone was slightly depressed at the beginning of the measurement period and continued with a steady decline to maximum losses of over 90 percent by early October. Very similar altitude profiles of ozone loss were observed by Hofmann et al. (1995) at the South Pole, suggesting the vortex wide character of these features.

If heterogeneous chemistry on volcanic aerosol was responsible for the low-altitude 1991–1993 ozone loss, then concomitant with the declining levels of volcanic aerosol, ozone should also return to its pre-Pinatubo pattern. In the right-hand panels of figure 2, 1994 and 1995 column ozone in 2-km layers is compared with the 1986–1990 record. The most obvious change occurs in the 10–12-km layer where, similar to the pre-Pinatubo period, relatively little ozone change is observed from late August through October. The low-ozone points in the 10–12-km layer in 1995 are all associated with days when the tropopause was above 12 km. A lessening of the ozone loss rate is also observed in the 12–14-km layer for 1994 and 1995. Although ozone in this layer is at or below the minima of the 1986–1990 period, ozone has increased from the minima observed in 1992 and 1993. A similar recovery of low-altitude ozone in 1994 was observed at the South Pole (Hofmann et al. 1995). In the 14–16-km region, recovery in 1994–1995 is not observed, indicating the importance of PSCs in this region.

From the column ozone amounts, ozone loss rates were calculated over the period when ozone displayed a fairly steady decline. The correlation between ozone loss and aerosol surface area is shown in figure 3 for the 10–12- and

12–14-km layers. The 14–16-km data show no such pattern, indicating again the relative unimportance of additional volcanic aerosol at these altitudes. Below 14 km, the dependence of ozone loss on surface area is quite steep. Approximately order-of-magnitude increases in surface area are required for a doubling of ozone loss rates.

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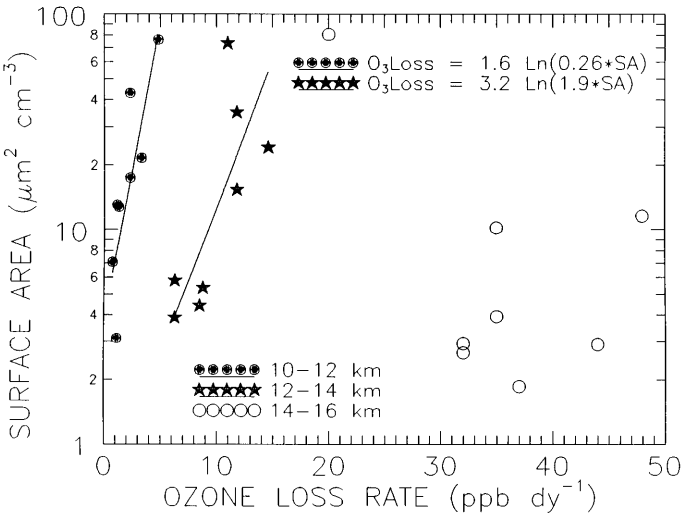

Figure 3. Ozone loss rates calculated from figure 2 plotted against average surface areas over the 2-km layers. The loss rates were converted from Dobson units per day to parts per billion per day (ppb dy^{-1}) using layer averaged temperature and pressure. Exponential fits to the 10–12- and 14–15-km layers are shown. Uncertainties in the ozone loss rates are estimated to be on the order of 30 percent for loss rates less than 5 ppb dy^{-1} decreasing toward 10 percent for higher loss rates.

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